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ATMOSPHERICALLY RELATED STUDIES OF $O(^1D)$ AND $O_2(b^1\Sigma_g^+)$

Prepared by:

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Molecular Physics Laboratory

SRI Project 4894
Contract No. NAGW-3669
MP 98-017

Prepared for:

National Aeronautics and Space Administration
Washington, DC 20546

Attn: Mary Mellott
Space Physics Division
Code SS

Approved by:

David R. Crosley, Director
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GOALS

The goals of this project are to investigate various aspects of the photochemistry of $O(^1D)$ and $O_2(b^1\Sigma_g^+)$ that are of relevance to the photochemistry and energy balance of the terrestrial atmosphere.

ACCOMPLISHMENTS

We report on two major areas of accomplishment this year:

1. The determination of the $O(^1D)$ yield from O_2 photodissociation across the width of the solar Lyman-alpha line.

Twenty years ago, we measured the $O(^1D)$ yield from O_2 photodissociation throughout the VUV spectral region.¹ The value of this parameter at the Lyman-alpha wavelength of 121.56 nm is quite important in the mesosphere, because this wavelength penetrates as low as 65 km and is an important source of oxygen atoms, and consequently, ozone. The significance of knowing the $O(^1D)$ yield in the process

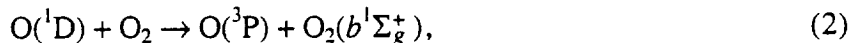


is that $O(^1D)$ disposes of its energy to the atmosphere by transfer to O_2/N_2 through a combination of electronic and vibrational energy transfer processes, whereas $O(^3P)$, once thermalized, is only lost reactively, by three-body recombination. Thus, the amount of $O(^1D)$ generated has consequences for the atmospheric energy balance.

In our earlier work,¹ we noted that the yield we extracted, 0.44 ± 0.05 , was situated on a rapidly changing portion of the yield spectrum, so the yield might be significantly different just a short wavelength interval away. This fact becomes potentially important when we consider that solar Lyman-alpha bears little resemblance in beam profile to a laboratory source. Solar Lyman-alpha is severely self-reversed,² and the intensity at line center, where the laboratory measurements were made, is only 1/3 that at the short- and long-wavelength peaks. The linewidth (FWHM) is on the order of 70 cm^{-1} , whereas the laboratory measurements were made with a 1-cm^{-1} -wide source. Therefore, we must remeasure the $O(^1D)$ yield, across the full width of the solar Lyman-alpha line. At the time of the original measurements, no source existed to make such a study possible.

In the interim, lasers have become common laboratory tools, and various optical techniques make it possible to construct a system providing tunable light in the Lyman-alpha region. This is accomplished by a four-wave mixing process, in which two photons from a 193 nm laser are subtractively combined with a visible dye-laser photon near 468 nm in a Kr/Ar or Kr/H₂ medium, resulting in several microjoules of laser radiation tunable in the 120-123 nm region.

Because $O(^1D)$ in O_2 has the convenient property of converting the energy of the atom to molecular excitation (an important atmospheric process),



the measured signal is the 0-0 band of the $O_2(b^1\Sigma_g^+ - X^3\Sigma_g^-)$ transition at 762 nm. By observing the intensity as a function of wavelength, and taking account of the changing O_2 absorption cross section with changing wavelength, we can extract the $O(^1D)$ yield over the region of interest.

In Figure 1 we show the data, which are normalized to our previous yield of 0.44 ± 0.05 . Also appearing in the figure is the solar Lyman-alpha profile, along with theoretical calculations carried out by our collaborators, Brenton Lewis' group at Australian National University. The short wavelength data of Figure 1 probably have an actual yield value of unity, which requires raising the value of our normalization point from 0.44 to 0.49. We consider this quite acceptable.

2. Investigations of the newly discovered $O_2(b^1\Sigma_g^+)$ nightglow from highly vibrationally excited levels.

Over the last six months, we have obtained new sky spectra data files from the Keck telescope *via* Don Osterbrock at UC Santa Cruz, and now 120 hours of data have been accumulated. Thus, we have been able to make large signal/noise improvements of the $O_2(b^1\Sigma_g^+ - X^3\Sigma_g^-)$ Atmospheric Band data that we are collecting. Our first publication on this topic was in Science,³ and the next one will appear in EOS.⁴

These astronomical spectra are routinely produced at the major telescopes, because it is important to subtract out the nightglow spectra from the spectra of stellar objects. The great advantage to aeronomers of having such spectra available is that they have far higher resolution than the usual aeronomic instruments, and produce such spectra over a wide wavelength range. We have data from 600 to 900 nm, taken with 0.02 nm resolution. This wavelength region is ideal for viewing the O_2 Atmospheric Band system, which is extensively used in aeronomy for a variety of reasons, but almost exclusively from the $b^1\Sigma_g^+ (v = 0)$ level. Higher levels have not been seen in the nightglow because quenching by O_2 is very fast.^{4,5} Therefore a highly sensitive spectrometer is needed. The HIRES echelle spectrometer on the Keck telescope is just such an instrument.

We have found vibrational levels in the $b^1\Sigma_g^+$ state as high as $v = 15$. Because no optical observations have been made beyond $v = 3$ in any system,⁶ the present investigation is a tremendous step forward. For a basic study, we can generate for the first time a reasonably accurate potential for almost the entire $b^1\Sigma_g^+$ state. In this effort we are aided by a recent electron energy loss spectrum of Allan,⁷ which permits extension of our data beyond $v = 15$, and is consistent with our data for lower-lying levels, although Allan's spectrum has an equivalent optical resolution of only 6 nm at 700 nm.

Because $O_2(b^1\Sigma_g^+)$ in the nightglow is generated principally from atom recombination, the observation of this large range of vibrational levels will provide information on how the recombination energy is degraded. From a practical point of view, we lose sight of this energy once it is collisionally removed from the Herzberg bands, and it only reappears in the $b^1\Sigma_g^+ (v = 0)$ level. With these new data, and particularly when collisional removal rates have been measured, we will be able to better understand atmospheric energy flow.

A new and very interesting observation is that the $v = 0, 1$ levels are unique, showing very high temperature components that are not associated with the 95 km nightglow region. The $b^1\Sigma_g^+ - X^3\Sigma_g^-$ 1-1 band shows high rotational lines compatible with a temperature of at least 500 K.

Such an observation could either reflect the local temperature of the emitting region, where the source would be reaction (2), or it might reflect the quasi-nascent production of $O_2(b^1\Sigma_g^+)$ by the same reaction. The half-quenching altitude of $b^1\Sigma_g^+ (v = 1)$ is ~ 150 km, so if the emission comes from this region or higher, the data may be showing the latter phenomenon. Wallace and Chamberlain⁸ reported just such an observation in 1959, i.e., high temperature in $b^1\Sigma_g^+ (v = 1)$, but in that case the source was auroral. However, the observations may well be related, because $O(^1D)$ is generated in aurorae.

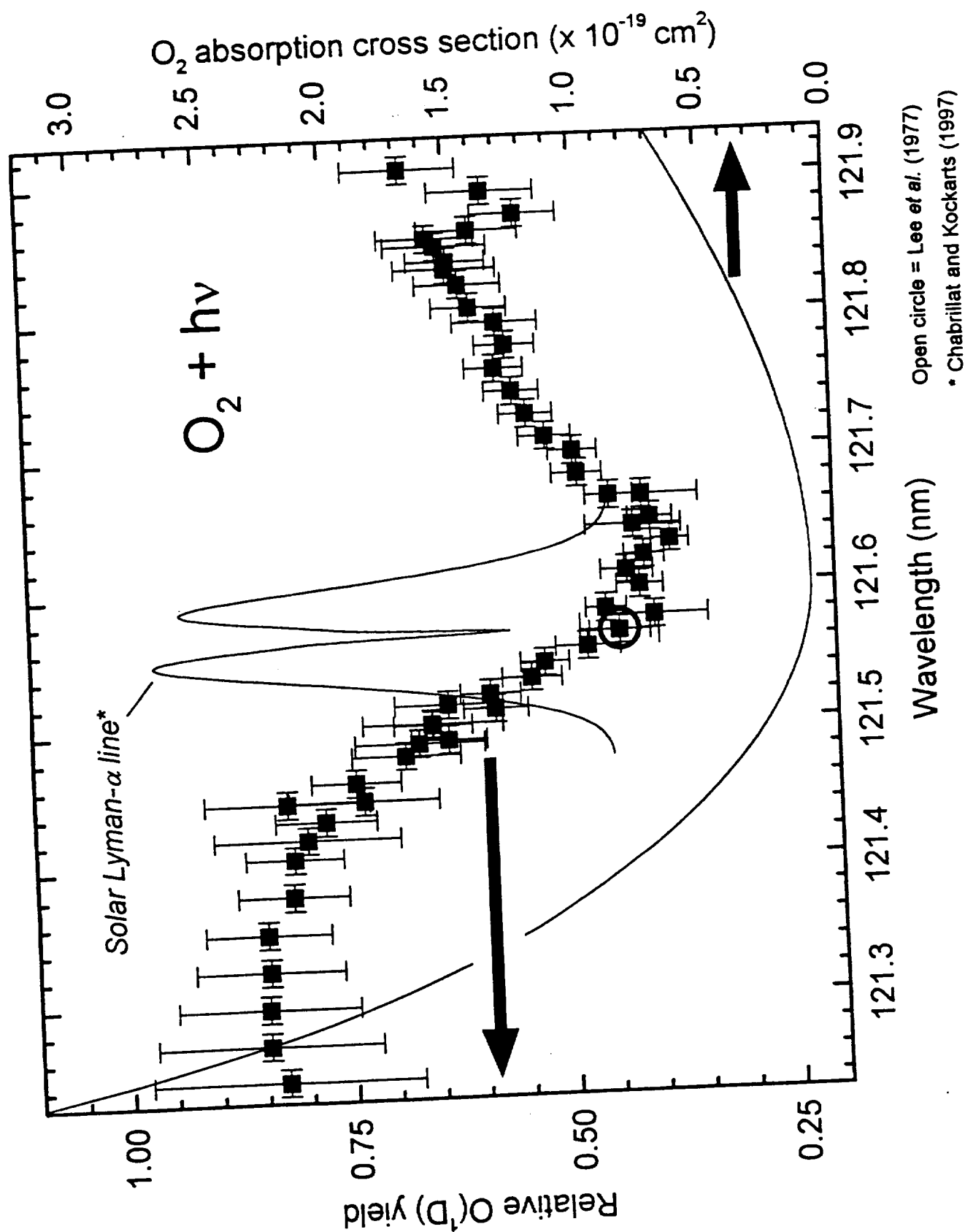
PLANS

For the third year of the grant, we propose to investigate the $b^1\Sigma_g^+$ yield of reaction (2). Our earlier value of 0.77 ± 0.23 ,⁹ which has been used for a long time, should be updated, and the error limits reduced. Current measurements in J. Barker's group at the University of Michigan have assigned a value closer to 0.9, and we will conduct a new evaluation.¹⁰

The technique to be used is to photodissociate ozone at 248 nm, generating both $O(^1D)$ and $O_2(a^1\Delta_g)$, with yields very close to 0.9. We will measure the $a^1\Delta_g$ yield by REMPI in an O_3/N_2 mixture and then replace the N_2 with O_2 , converting $O(^1D)$ to $O_2(b^1\Sigma_g^+)$ via reaction (2). The collisional fate of the $b^1\Sigma_g^+$ state with almost all known colliders is to generate the $a^1\Delta_g$ state.¹¹ By adding a small amount of CO_2 , all $b^1\Sigma_g^+$ can be converted to $a^1\Delta_g$ (with minimal quenching of the $O(^1D)$ by CO_2). Thus, the amount of $a^1\Delta_g$ before and after CO_2 addition should lead to a value of the $O(^1D)$ yield in reaction (2).

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THE YIELD OF $O(^1D)$ FROM O_2 PHOTODISSOCIATION NEAR LYMAN-ALPHA